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Crystal structure of 3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine: the acaricide clofentezine

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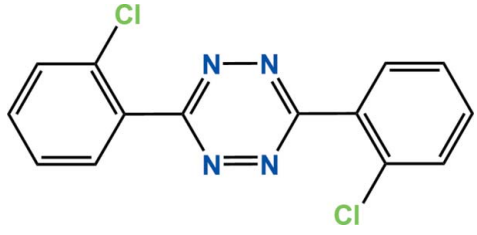
The whole molecule of the title compound, $C_{14}H_8Cl_2N_4$, is generated by inversion symmetry. The dihedral angle between the 2-chlorophenyl ring and the tetrazine ring is 47.65 (5)°. In the crystal, molecules are linked by slipped parallel π–π interactions [centroid–centroid distance = 3.8199 (5), normal distance = 3.3127 (8), slippage 1.902 Å] forming columns along the *a*-axis direction.

Keywords: crystal structure; clofentezine; acaricide; π–π interactions.

CCDC reference: 1026062

1. Related literature

For information on the toxicity and acaricidal properties of the title compound, which is used in plant protection for the control of spider mites on a wide range of crops, see: Zhao *et al.* (1996); Ay & Ebru Kara (2011). For the structures of the *m*- and *p*-isomers, see: Infantes *et al.* (2003).



2. Experimental

2.1. Crystal data

$C_{14}H_8Cl_2N_4$
M_r = 303.14
Monoclinic, $P2_1/n$
a = 3.8199 (4) Å
b = 14.0706 (16) Å
c = 12.1066 (15) Å
β = 97.715 (3)°
V = 644.82 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.50 mm^{-1}
T = 173 K
0.45 × 0.09 × 0.06 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.808, T_{max} = 0.971
4197 measured reflections
1456 independent reflections
1222 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.07
1456 reflections
91 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: NK2226).

References

Ay, R. & Ebru Kara, F. (2011). *Insect Sci.* **18**, 503–511.
Brandenburg, K. (2010). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Infantes, L., Mahon, M. F., Male, L., Raithby, P. R., Teat, S. J., Sauer, J. R., Jagerovic, N., Elguero, J. & Motherwell, S. (2003). *Helv. Chim. Acta*, **86**, 1205–1221.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhao, G., Liu, W. & Knowles, C. O. (1996). *Exp. Appl. Acarol.* **20**, 215–222.

supporting information

Acta Cryst. (2014). E**70**, o1135 [doi:10.1107/S1600536814021291]

Crystal structure of 3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine: the acaricide clofentezine

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S1. Comment

Clofentezine, $C_{14}H_8Cl_2N_4$, is an acaricide that is used in plant protection for the control of spider mites on a wide range of crops (Zhao *et al.*, 1996; Ay & Ebru Kara, 2011), and its crystal structure is reported herein. This molecule is located on a centre of symmetry, and a half molecule constitutes the asymmetric unit (Scheme 1, Fig. 1). The dihedral angle between a mean plane of the 2-chlorophenyl ring (r.m.s. deviation 0.0109 Å) and a mean plane of the tetrazine ring (r.m.s. deviation 0.0002 Å) is 47.65 (5)°. All bond lengths and bond angles are normal and comparable to those observed in the crystal structure of *m*- and *p*-isomers (Infantes *et al.*, 2003).

In the crystal structure, weak intermolecular face-to-face $\pi\cdots\pi$ interactions between the tetrazine ring systems [$Cg1\cdots Cg1^{ii}$, 3.8199 (5) Å] and the phenyl ring systems [$Cg2\cdots Cg2^{ii}$, 3.8199 (5) Å] link molecules in one-dimensional packing structure along [100] (*Cg*1 and *Cg*2 are the centroids of the N1···C1 and C2···C7 rings, respectively) [for symmetry codes: (ii), -*x* + 1, -*y* + 1, -*z* + 1].

S2. Experimental

The title compound was purchased from the Dr Ehrenstorfer GmbH Company. Slow evaporation of a solution in $CHCl_3$ gave single crystals suitable for X-ray analysis.

S3. Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.95 Å, $U_{iso} = 1.2U_{eq}$(C) for aromatic C—H groups.

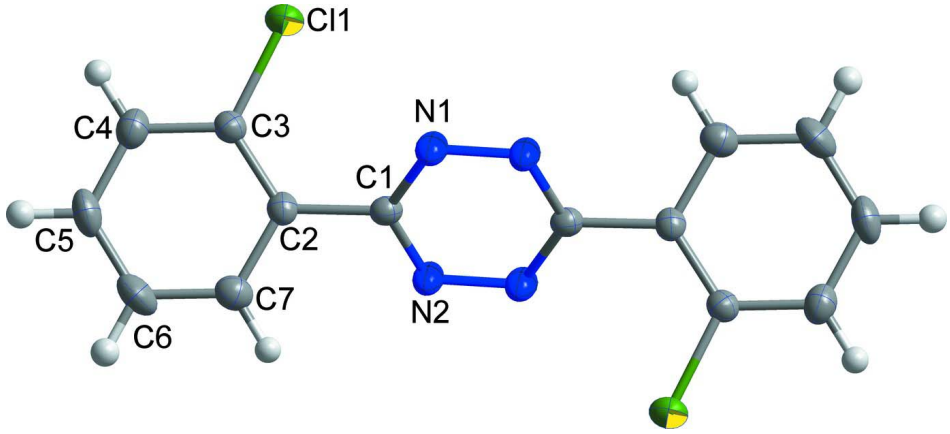

Figure 1

The asymmetric unit of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

3,6-bis(2-Chlorophenyl)-1,2,4,5-tetrazine

Crystal data

$C_{14}H_8Cl_2N_4$
$M_r = 303.14$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 3.8199\ (4)$ Å
$b = 14.0706\ (16)$ Å
$c = 12.1066\ (15)$ Å
$\beta = 97.715\ (3)°$
$V = 644.82\ (13)$ Å^3
$Z = 2$
$F(000) = 308$
$D_x = 1.561$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1312 reflections
$\theta = 2.2–27.0°$
$\mu = 0.50$ mm^{-1}
$T = 173$ K
Plate, red
0.45 × 0.09 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.808$, $T_{max} = 0.971$
4197 measured reflections
1456 independent reflections
1222 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.4°$, $\theta_{min} = 2.2°$
$h = -4\rightarrow4$
$k = -14\rightarrow18$
$l = -15\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 1.07$
1456 reflections
91 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.299P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.72153 (14)	0.44093 (3)	0.68048 (4)	0.03196 (18)
N1	1.1350 (5)	0.45432 (11)	0.91567 (14)	0.0288 (4)
N2	0.8626 (5)	0.58937 (11)	0.98682 (13)	0.0281 (4)
C1	0.9976 (5)	0.54235 (12)	0.90522 (16)	0.0221 (4)
C2	1.0066 (5)	0.59412 (12)	0.79914 (15)	0.0219 (4)
C3	0.9028 (5)	0.55442 (12)	0.69426 (16)	0.0229 (4)
C4	0.9276 (5)	0.60556 (14)	0.59725 (17)	0.0310 (5)
H4	0.8507	0.5782	0.5264	0.037*
C5	1.0657 (6)	0.69676 (15)	0.60499 (19)	0.0355 (5)
H5	1.0929	0.7310	0.5390	0.043*
C6	1.1638 (6)	0.73814 (14)	0.7076 (2)	0.0349 (5)
H6	1.2533	0.8012	0.7122	0.042*
C7	1.1319 (5)	0.68778 (14)	0.80399 (18)	0.0296 (4)
H7	1.1959	0.7172	0.8744	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0376 (3)	0.0258 (3)	0.0319 (3)	−0.0065 (2)	0.0026 (2)	−0.00350 (19)
N1	0.0405 (10)	0.0240 (8)	0.0224 (8)	0.0090 (7)	0.0064 (7)	0.0001 (6)
N2	0.0410 (10)	0.0225 (7)	0.0214 (8)	0.0082 (7)	0.0060 (7)	0.0006 (6)
C1	0.0238 (9)	0.0204 (8)	0.0220 (9)	0.0013 (7)	0.0022 (7)	−0.0021 (7)
C2	0.0219 (9)	0.0218 (8)	0.0228 (9)	0.0040 (7)	0.0053 (7)	0.0013 (7)
C3	0.0227 (9)	0.0212 (9)	0.0251 (10)	0.0013 (7)	0.0044 (8)	0.0007 (7)
C4	0.0340 (11)	0.0353 (11)	0.0238 (10)	0.0043 (9)	0.0046 (8)	0.0035 (8)
C5	0.0380 (12)	0.0340 (11)	0.0362 (12)	0.0042 (9)	0.0109 (10)	0.0170 (9)
C6	0.0326 (11)	0.0222 (9)	0.0506 (14)	−0.0005 (8)	0.0078 (10)	0.0084 (9)
C7	0.0297 (11)	0.0249 (9)	0.0338 (11)	0.0009 (8)	0.0029 (9)	−0.0006 (8)

Geometric parameters (Å, º)

Cl1—C3	1.7397 (18)	C3—C4	1.391 (3)
N1—N2^{i}	1.330 (2)	C4—C5	1.386 (3)
N1—C1	1.345 (2)	C4—H4	0.9500
N2—N1^{i}	1.330 (2)	C5—C6	1.378 (3)
N2—C1	1.348 (2)	C5—H5	0.9500

C1—C2	1.481 (3)	C6—C7	1.385 (3)
C2—C3	1.395 (3)	C6—H6	0.9500
C2—C7	1.401 (3)	C7—H7	0.9500
N2^{i}—N1—C1	117.74 (16)	C5—C4—H4	120.3
N1^{i}—N2—C1	117.78 (16)	C3—C4—H4	120.3
N1—C1—N2	124.49 (17)	C6—C5—C4	120.48 (19)
N1—C1—C2	118.72 (16)	C6—C5—H5	119.8
N2—C1—C2	116.74 (16)	C4—C5—H5	119.8
C3—C2—C7	117.95 (17)	C5—C6—C7	119.98 (19)
C3—C2—C1	123.74 (16)	C5—C6—H6	120.0
C7—C2—C1	118.30 (17)	C7—C6—H6	120.0
C4—C3—C2	121.19 (17)	C6—C7—C2	120.95 (19)
C4—C3—Cl1	117.72 (15)	C6—C7—H7	119.5
C2—C3—Cl1	121.05 (14)	C2—C7—H7	119.5
C5—C4—C3	119.4 (2)		
N2^{i}—N1—C1—N2	0.1 (3)	C7—C2—C3—Cl1	−176.46 (14)
N2^{i}—N1—C1—C2	177.28 (17)	C1—C2—C3—Cl1	4.6 (3)
N1^{i}—N2—C1—N1	−0.1 (3)	C2—C3—C4—C5	1.5 (3)
N1^{i}—N2—C1—C2	−177.33 (17)	Cl1—C3—C4—C5	179.03 (15)
N1—C1—C2—C3	47.7 (3)	C3—C4—C5—C6	−2.7 (3)
N2—C1—C2—C3	−134.8 (2)	C4—C5—C6—C7	1.4 (3)
N1—C1—C2—C7	−131.16 (19)	C5—C6—C7—C2	1.2 (3)
N2—C1—C2—C7	46.3 (3)	C3—C2—C7—C6	−2.3 (3)
C7—C2—C3—C4	1.0 (3)	C1—C2—C7—C6	176.64 (18)
C1—C2—C3—C4	−177.93 (18)		

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+2.